

Executive Summary

What is the ozone weekend effect?

The “ozone weekend effect “ refers to the interesting observation that ozone measurements in some locations are typically higher on weekends compared to weekdays. This is somewhat surprising because smog-forming emissions mostly come from sources, such as cars, trucks, and factories, that could be expected to produce lower total emissions on weekends compared to weekdays.

Why was this report written?

This report was written at the request of the Air Resources Board because the ozone weekend effect is more than a scientific curiosity. It has become an important regulatory and scientific issue because it has been offered by some as evidence that major reductions of NO_x (nitrogen oxides) emissions would be counter-productive for reducing ambient ozone levels at this time.

For example, in November 1998, the Air Resources Board adopted Low Emission Vehicle regulations (LEV-II) aimed at reducing emissions, including NO_x, from motor vehicles. At the LEV-II hearing, the ozone weekend effect was presented in public testimony as justification for deleting the standards that required lower NO_x emissions. At that time, the Board directed the CARB staff to investigate the scientific evidence relating to the ozone weekend effect and evaluate its implications concerning NO_x reductions as an ozone control strategy.

Before looking further into the ozone weekend effect, a little history is helpful to set the context of NO_x reductions in California’s current ozone control strategy.

Are NO_x reductions a new feature of ozone control strategies?

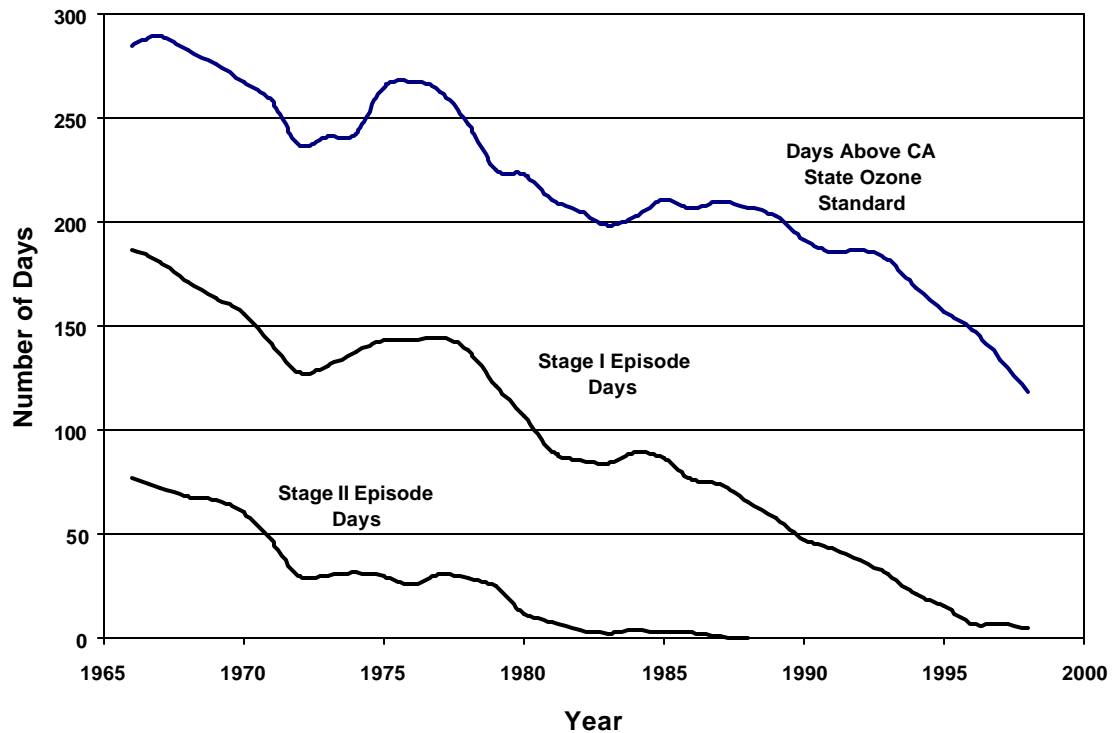
No. A strategy of concurrent reductions of the primary ozone precursors, volatile organic compounds (VOCs) and NO_x, has been used for more than twenty years to reduce ozone concentrations in California’s ambient air.

Have concurrent reductions of VOCs and NO_x been effective at reducing ozone concentrations?

Yes. Concurrent reductions of VOCs and NO_x have been very successful at reducing ozone concentrations in California. From the mid-1970’s into the 21st century, the ozone control strategy implemented in the South Coast Air Basin (SoCAB) included reductions of both VOC emissions and NO_x emissions. Early NO_x reductions were achieved by statewide controls on emissions from motor vehicles combined with local controls on emissions from industrial sources, such as cement kilns.

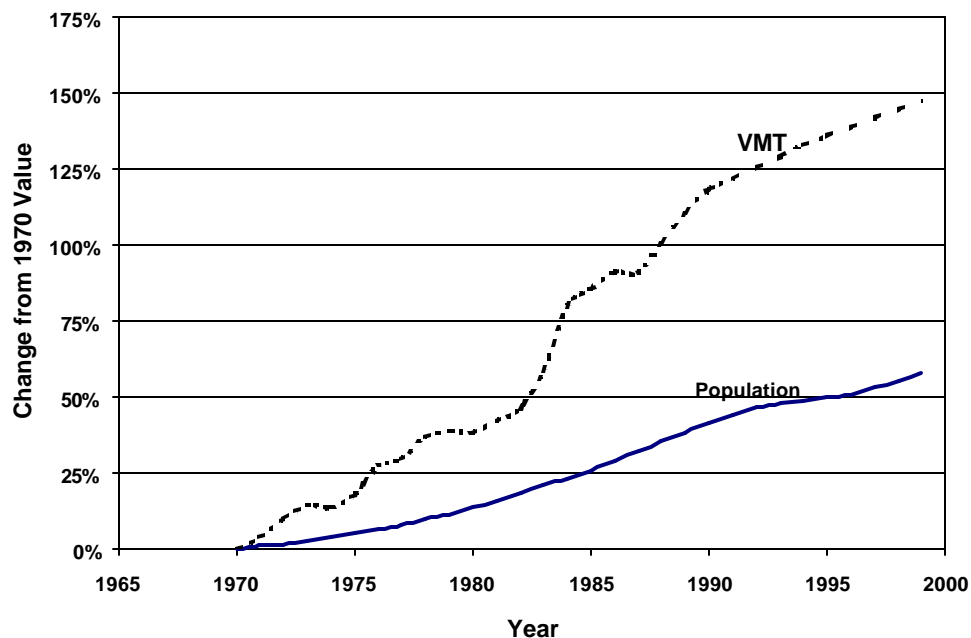
Figure 1 shows the historic success of concurrent VOC and NO_x reductions in the SoCAB. Unhealthful concentrations of ozone in the basin have been reduced

Figure 1. Trends for the number of days per year when the California Ambient Air Quality Standard for ozone was exceeded * and when Stage I ** and Stage II * ozone episodes occurred within the South Coast Air Basin.**



Notes: Early ozone values represent "total oxidant" adjusted to "ozone equivalent". Trends are 3-year moving averages based on annual values for 1965 - 1999.
 * Exceedances of the CA hourly ozone standard (95 ppb or more) decreased more than 60 percent.
 ** Stage I episodes, max-hour ozone of 200 ppb or more, decreased more than 95 percent.
 *** Stage II episodes, max-hour ozone 350 ppb or more, were eliminated in 1989.

Figure 2. Percent growth in population and vehicle miles traveled from 1970 to 1999 in the South Coast Air Basin.



dramatically. These improvements have occurred despite rapid population growth and even faster growth in vehicle use as shown in Figure 2.

Are NO_x emission reductions only relevant to ozone?

No. Secondary products of NO_x emissions contribute to ambient levels of several pollutants in addition to ozone. Some of these pollutants, such as, fine particulate matter (PM₁₀ and PM_{2.5}), nitrogen dioxide (NO₂), nitric acid, peroxy-acyl-nitrates (PANs), and some nitro-polycyclic compounds, are known to be detrimental to human beings, to the environment, or to both.

For some of these compounds, data are scarce and specific changes attributable to reductions in NO_x emissions are difficult to identify. Measurements of NO₂, however, show that annual maximum NO₂ concentrations at 15 sites in the SoCAB were reduced by 32% to 64% from 1980 to 1998. The Basin did not attain the state 1-hour standard for NO₂ until the mid-1990s. In addition to NO₂, it is likely that other secondary products of NO_x emissions have declined in the last 20 years in the SoCAB.

Because multiple pollutants are affected by NO_x reductions, they are often considered together rather than separately when developing pollution control plans. Nevertheless, the remainder of this summary primarily considers the ozone weekend effect and its relevance to NO_x reductions as an ozone control measure.

Have concurrent reductions of VOCs and NO_x been effective only on weekdays?

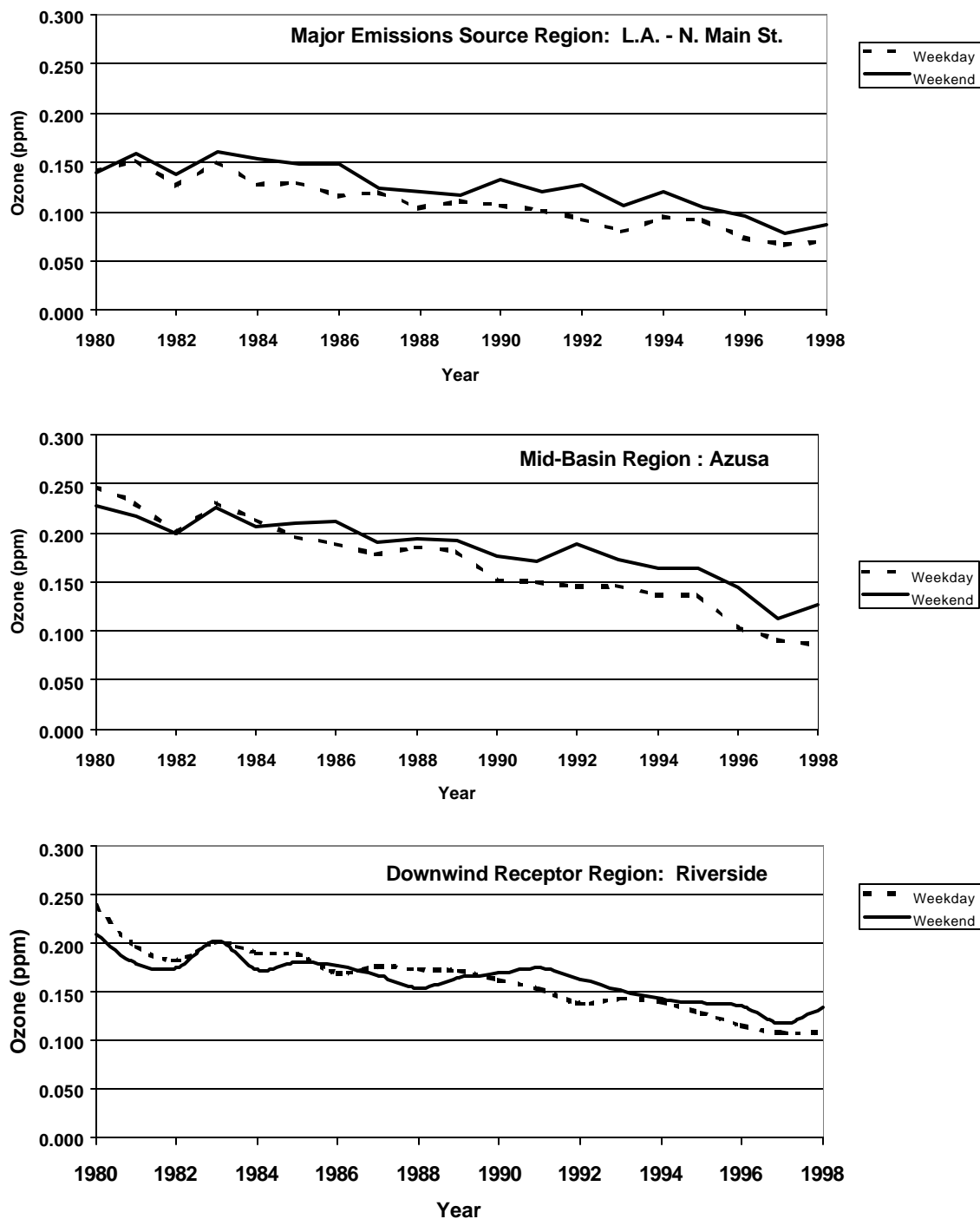
No. Concurrent reductions of VOCs and NO_x have been effective at reducing ozone concentrations on all days of the week, including weekends. Figure 3 shows trends for weekdays and for weekends at three locations in the SoCAB. Both weekdays and weekends show substantial improvements at all three locations. The trends for other sites in the SoCAB show similar results.

Is the ozone weekend effect real?

Yes. In some locations, ozone concentrations are typically higher on weekends despite indications that smog-forming emissions of VOCs and NO_x are almost certainly lower on weekends (especially on Sunday) for these same locations. The ozone weekend effect is seen in Figure 3; it occurs when the solid line is above the dotted line in the graphs.

Measured concentrations of VOCs and NO_x in the ambient air represent the integrated impact of many sources, and these concentrations usually decrease on weekends at most monitoring sites. The decrease tends to be moderate on Saturday and more substantial on Sunday. In the SoCAB during daylight hours (6 a.m. to 8 p.m.), VOC concentrations (inferred from measured CO values) decrease about 10% on Saturday and 25% on Sunday with respect to midweek levels. Similarly,

Figure 3. Ozone trends from 1980 through 1998 for weekdays and weekends at Azusa, L.A. - North Main St., and Riverside in the South Coast Air Basin.
(Ozone is the mean of the 2nd - 11th highest daily maximum ozone concentrations each year.)



measured NO_x concentrations decrease about 25% on Saturday and 40% on Sunday. Nevertheless, ozone is routinely higher on weekends throughout the SoCAB.

Does the ozone weekend effect occur everywhere?

No. The ozone weekend effect presently occurs at most, if not all, of the monitoring sites in the Los Angeles and San Francisco metropolitan areas, based on measurements during the ozone seasons of 1996 through 1998. However, the ozone weekend effect is absent or negligible at most sites in the Sacramento and San Joaquin Valleys.

This report primarily, but not exclusively, considers data from the Los Angeles area because of the greater abundance of data available for analysis.

How big is the ozone weekend effect?

Based on data from 1996 through 1998, typical ozone weekend effects in four major areas of California are the following:

- South Coast Air Basin – 22 ppb or 32% higher than Friday ozone
- San Francisco Bay Area Air Basin – 9 ppb or 25% higher than Friday ozone
- Sacramento Metropolitan area – 5 ppb or 8% higher than Friday ozone (not statistically significant)
- San Joaquin Valley Air Basin – 4 ppb or 6% higher than Friday ozone (not statistically significant)

For comparison, the levels of the national and state one-hour standards for ozone are 120 ppb and 90 ppb respectively.

In these four regions, the ozone weekend effect tends to be smallest at those sites that measure the highest ozone concentrations.

Do other air pollutants show a weekend effect?

Yes, but usually in the opposite direction from ozone.

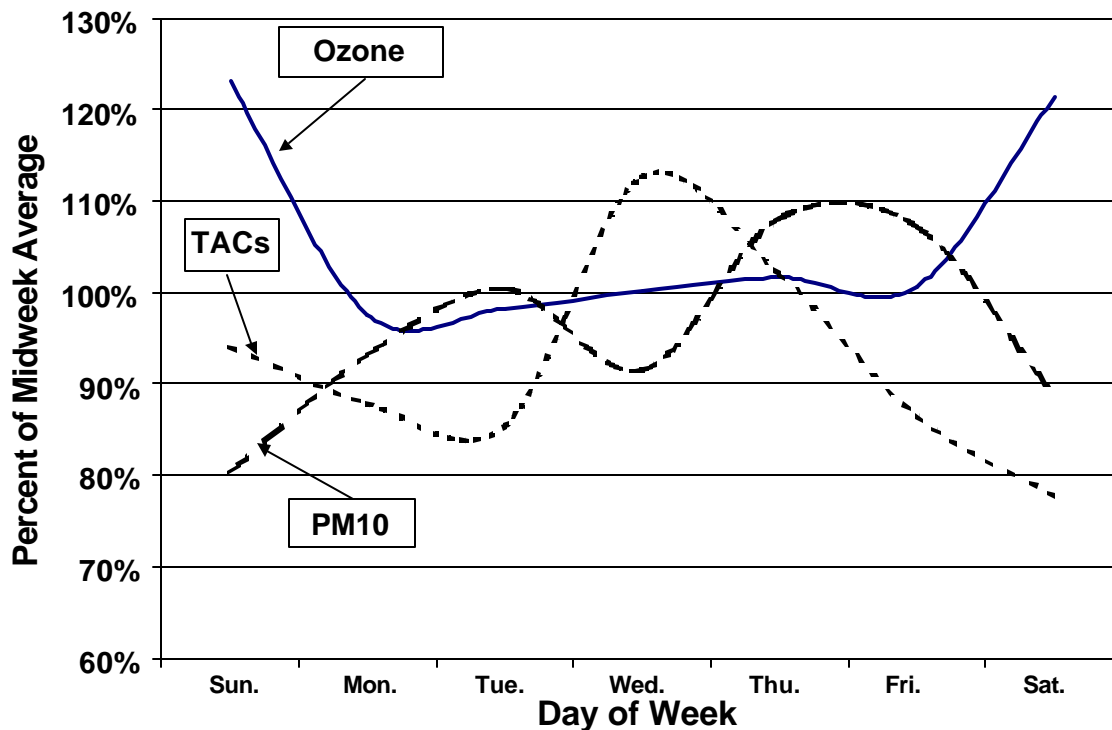
Although this report emphasizes ozone, the day-of-week behavior of some other pollutants was examined (Figure 4). Analyses of recent data for nitrogen dioxide (NO₂), carbon monoxide (CO), particulate matter (PM₁₀ and PM_{2.5}), and six high-risk toxic air contaminants indicate that these pollutants tend to decrease or remain the same on weekends compared to weekdays.

- Daily maximum (peak) concentrations of NO₂ and CO are lower on weekends compared to weekdays. In some locations, however, these pollutants may meet or exceed the weekday levels during some mid-day or nighttime hours.
- Concentrations of PM₁₀ and PM_{2.5} are typically lower on weekends compared to weekdays. One component of PM is particularly relevant to the

issues involved with the ozone weekend effect. Particulate nitrates are secondary products of NO_x and other emissions. Although it is likely that particulate nitrates decrease on weekends, the available data are ambiguous and appear to be affected by factors that obscure the effects of day-of-week differences in emissions.

- Concentrations of benzene, 1,3-butadiene, and perchloroethylene generally decrease on weekends compared to weekdays.
- Concentrations of formaldehyde, acetaldehyde, and carbon tetra-chloride did not display consistent differences between weekdays and weekends.

Figure 4. Day-of-week profiles for ozone, particulate matter, and cancer risk (potency-weighted) for six toxic air contaminants in the South Coast Air Basin.



Notes:

1. Ozone is the average value for 22 sites in the SoCAB. The value for each site is the average of the daily maximum ozone concentrations during the May-October ozone seasons of 1996 – 1998 by day of the week.
2. Particulate matter is the average value for 17 sites in the SoCAB. The value for each site is the average of all values during 1996 – 1998 by day of week.
3. The TAC values are total cancer risk estimates for six TACs (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, perchloroethylene, and carbon tetrachloride) using average values for 1996 – 1998.
4. The dip in concentration for PM10 on Wednesdays appears to be an artifact of sampling procedures for SSIs. Observations using TEOM instruments do not exhibit this behavior.

Why do some believe the ozone weekend effect implies that major reductions in NO_x emission reductions will be counter-productive for reducing ozone?

Despite the long-term record of success for concurrent reductions of VOCs and NO_x in California, some people assert that further, significant NO_x reductions will be counter-productive for controlling ozone. That is, they believe greater success will be achieved with only VOC reductions. Their reasoning, called the **NO_x-reduction hypothesis** in this report, includes three points.

First, smog chamber experiments show that NO_x sometimes promotes and sometimes restricts ozone formation depending on the relative abundance of VOCs. The abundance of VOCs relative to NO_x is characterized by the VOC/NO_x ratio. In experiments where the VOC/NO_x ratio is less than 8 to 10, reducing NO_x tends to increase ozone formation. However, when the VOC/NO_x ratio is higher than 8 to 10, reducing NO_x tends to decrease ozone formation.

Second, VOC/NO_x ratios at the surface are less than 8 to 10 in most of the SoCAB. If this complex air basin acts like a simple smog chamber, then reducing NO_x emissions should (hypothetically) promote ozone formation. On weekends, NO_x emissions are reduced substantially, along with smaller reductions of VOC emissions. With lower NO_x and higher ozone on weekends, the real world and the laboratory appear to correspond.

Finally, opponents of NO_x -reducing regulations propose that the periodic NO_x reductions on weekends mimic the steady NO_x reductions from strategic regulations. Because the periodic NO_x reductions are associated with ozone increases, they assert that strategic NO_x reductions would slow the rate of progress that would otherwise be earned through VOC reductions.

Are there other possible causes of the ozone weekend effect?

Yes. The NO_x-reduction hypothesis is only one possible explanation of the ozone weekend effect. This report explores the NO_x-reduction hypothesis along with several alternative hypotheses concerning the cause or causes of the ozone weekend effect. Contrary to the NO_x reduction hypothesis, the alternative hypotheses do not imply that strategic NO_x reductions would be counter-productive for reducing ozone.

The various hypotheses are not mutually exclusive; each could explain a large or small part of the overall effect. Each additional hypothesis is described below in hypothetical terms only. Later in this summary, each hypothesis is evaluated in light of the available data.

- **NO_x-timing hypothesis:** This hypothesis assumes that the timing of NO_x emissions on weekends is very different from weekdays. The total NO_x emissions on weekends may be the same or less than on weekdays, but the timing is assumed to make the weekend emissions more efficient at

producing ozone, leading to higher observed ozone concentrations on weekends.

- **Carryover near the ground hypothesis:** This hypothesis assumes that the volume of traffic is greater on Friday and Saturday nights compared to other nights of the week. This extra traffic is assumed to emit more VOCs and NO_x during the nighttime hours between Friday and Saturday and between Saturday and Sunday. The additional emissions are assumed to remain near the ground and help form extra ozone during the daylight hours on Saturday and Sunday.
- **Carryover aloft hypothesis:** This hypothesis assumes that large reservoirs of ozone and ozone-forming pollutants commonly persist overnight above the cool layer of air near the surface. On the following day, these pollutants are assumed to mix down to the surface as the surface is warmed by the sun. The pollutants that mix down from aloft are assumed to interact with fresh surface emissions in such a way that ozone measured at the surface on weekends is greater than the ozone measured at the surface on weekdays.
- **Increased weekend emissions hypothesis:** This hypothesis assumes that the total emissions of VOCs and the total emissions of NO_x from all sources (human activities and natural) are actually greater on weekends compared to weekdays. Therefore, the higher concentrations of ozone observed on weekends are assumed to reflect the higher emissions of ozone precursors.
- **Soot and sunlight hypothesis:** This hypothesis assumes that there is more soot in the atmosphere on weekdays than on weekends. Soot particles can absorb the ultra-violet sunlight that drives ozone-forming reactions in the atmosphere. Therefore, it is assumed that the ultra-violet solar radiation needed to initiate the ozone forming reactions is absorbed on weekdays more than on weekends. The larger amount of available ultra-violet radiation on weekends is assumed to contribute to higher ozone concentrations on weekends.

Do the available data demonstrate which hypotheses are correct?

No. Despite California's ambitious programs in air quality monitoring, emissions inventories, and atmospheric research, crucial gaps in the available data must be filled before definitive conclusions can be reached in this regard.

Existing data are not sufficient because ongoing programs and special studies are usually designed to address typical days or extreme "episode" days. In general, these programs have not been designed to explain why ozone concentrations might differ (as they do) on different days of the week.

Current air monitoring data are sufficient to demonstrate that the ozone weekend effect is real and to suggest possible causes. However, this study shows that additional data are needed before the cause or causes of the ozone weekend effect can be determined.

Do the available data indicate which hypotheses are plausible?

Yes. Analyses of the available data indicate that several hypotheses are plausible and each may explain a significant portion to the periodic ozone weekend effect. A plausible hypothesis, however, is not necessarily applicable to California's long-term ozone control strategy.

- The **NO_x-reduction hypothesis** is plausible. The VOC/NO_x ratios from surface measurements are generally in the "VOC-limited" range. Air quality data indicate that NO_x emissions are reduced on weekends proportionally more than VOC emissions. Therefore, higher ozone on weekends compared to weekdays could be a direct result of lower NO_x emissions.
- The **NO_x-timing hypothesis** is plausible. Traffic is the single largest source of NO_x emissions in the South Coast Air Basin. On weekday mornings, rush-hour traffic produces large amounts of NO_x, leading to daily-maximum concentrations of NO_x between 6 a.m. and 9 a.m. On weekends, however, the morning traffic is much lighter; NO_x emissions and peak concentrations between 6 a.m. and 9 a.m. are substantially lower on weekends. By mid-day, however, traffic volumes and NO_x emissions are closer to weekday levels.

This timing difference is potentially important because laboratory experiments indicate that NO_x emitted later in the day can produce ozone more efficiently. Higher ozone concentrations on weekends may result from differences in the timing of NO_x emissions.

- The **carryover near the ground hypothesis** is only marginally plausible, because it probably does not contribute significantly to the ozone weekend effect. Traffic activity data for freeways show that the volume of traffic on Friday and Saturday evenings is greater than it is on other days of the week. This activity occurs after surface temperatures begin cooling in the evening. Therefore, the extra emissions should remain near the ground and could participate in smog-forming processes following sunrise the next day.

However, ground-level measurements of NO_x and VOCs at sunrise indicate that concentrations of these pollutants at the surface are lower on weekends compared to weekdays. These observations indicate that the amounts of smog-forming emissions that carry over near the surface from Friday and Saturday nights is small relative to the amount of fresh emissions on weekday mornings. Therefore, carryover near the surface is not likely to be a significant cause of the ozone weekend effect.

- The **carryover aloft hypothesis** is plausible. During the Southern California Ozone Study in 1997, measurements aloft (200 to 5000 feet or more) found large reservoirs of ozone that carried over from one day to the next. A recent study of carryover aloft in the northeast states indicates that surface ozone concentrations can be strongly affected, even dominated, by materials that carry over aloft.

Low NO_x emissions on weekends may interact with ozone and other materials aloft so that ozone levels on weekends are higher compared to weekdays. On weekdays, large amounts of fresh NO_x emitted at the surface may destroy ozone and radicals that mix down from aloft, thereby limiting their contribution to surface ozone concentrations. On weekends, however, NO_x concentrations can be significantly lower, so less ozone from aloft is destroyed, and ozone from aloft contributes to higher ozone measurements at the surface on Saturday and Sunday.

- The **increased weekend emissions hypothesis** is not plausible as a significant contributor to the ozone weekend effect. The proposition that emissions of VOCs and NO_x increase on weekends is not consistent with most of the available data. Nevertheless, emissions in some areas may increase on weekends. For example, Lynwood, in South Central Los Angeles, has the highest carbon monoxide concentrations in the U.S. and records higher CO during mid-day hours on Saturdays than any other day of the week. Ozone tends to be highest at all sites on Sundays, however, when CO at Lynwood does not exceed the weekday levels. Better understanding of emissions in South Central L.A. and other regions is an important objective of activity studies. Data from such studies may reveal that emissions on weekends increase in selected locations and contribute to local variations in the ozone weekend effect.
- The **soot and sunlight hypothesis** is plausible theoretically, but accurate data on light absorption and light scattering are scarce. Both laboratory experiments and ambient measurements are needed. Daily simultaneous measurements of emissions and ambient levels of PM_{2.5} (elemental carbon in particular) and ultra-violet sunlight are needed to clarify the contribution of this hypothesis to the ozone weekend effect.

Because motor vehicles are a major source of soot particles, it is plausible that soot particles are less abundant on weekends compared to weekdays. If so, ultra-violet sunlight should be more available on weekends to drive ozone-forming processes. Therefore, ozone-forming reactions may be more vigorous on weekends and contribute to higher ozone on Saturday and Sunday.

This hypothesis was proposed but not investigated due to limited data.

In summary, analyses of existing databases suggest that several possible causes of the ozone weekend effect are plausible. However, currently available data are not sufficient to separate and quantify the contributions of the alternative causes.

What are the next steps?

The ARB and other interested parties are continuing to investigate the ozone weekend effect. The Technical Support Document for this report lists several projects sponsored by government and/or private institutions. The ARB staff is preparing plans for a significant study of emissions differences by day of week. These efforts

acknowledge that understanding the causes of the ozone weekend effect and quantifying their respective contributions will require information that is not available today.

A research program involving field studies, laboratory experiments, and modeling exercises is recommended to fill this need. An outline of research options is provided in Chapter 5 of this report as a starting point for discussion and planning. Major elements of this research, with reference to the South Coast Air Basin, are the following:

- **Field studies**

Ambient measurements of VOCs and nitrogen-containing compounds are needed with high resolution in space and time, both at the surface and aloft.

Because the alternative hypotheses concerning the causes of the ozone weekend effect involve time-dependent changes in emissions and atmospheric conditions, hourly measurements are highly desirable. Because the ozone weekend effect is not uniform throughout a region, data for many locations are also highly desirable. Measurements “aloft” (three-dimensional space) are scarce but potentially vital for understanding the ozone weekend effect.

Measurements of VOCs (ppbC) that account for all gaseous carbon compounds are needed. Recent improvements in monitoring methods could make such measurements feasible on an hourly basis at many locations.

Routine NO_x measurements today are not specific for the sum of NO and NO_2 . Instead, they include portions of other compounds, such as, N_2O_5 , HNO_3 , and PAN. These routine measurements also lack the precision needed to characterize VOC/ NO_x ratios with satisfactory accuracy during the mid-day hours when ozone is high. New monitoring methods, however, may allow highly precise and specific, artifact free measurements of NO, NO_2 , nitrate radical (NO_3), and HNO_3 . Such data could help resolve the causes of the ozone weekend effect.

Measurements of PAN, nitro-PAHs, particulate nitrates, and other compounds containing nitrogen are desirable for understanding the ozone weekend effect and for understanding the impact of NO_x emission reductions on multiple air pollutants.

To address these needs satisfactorily will require a significant investment in time and resources to carry out the appropriate field studies.

- **Laboratory experiments**

Some of the chemical mechanisms currently used in computer models to investigate the response of ozone to changes in VOC and NO_x emissions may overestimate ozone production when NO_x concentrations are low. If so, appropriate modifications to these mechanisms may require new smog-chamber studies under low- NO_x conditions.

Previous laboratory experiments concerning the timing of NO_x emissions may need to be corroborated and expanded. Present generation smog chambers reduce experimental artifacts compared to earlier chambers, and this may alter the earlier results significantly.

Other laboratory investigations may be needed to resolve the causes of the ozone weekend effect.

- **Modeling exercises**

Computer models that simulate photochemical smog become more sophisticated with each passing year. Nevertheless, using these models to investigate the ozone weekend effect presents several uncommon challenges. Examples include the following:

1. Hourly emissions inventories for weekend days are not generally available.
2. Appropriate initial conditions and boundary conditions may not be known satisfactorily.
3. Some chemical mechanisms may not perform adequately under low-NO_x (weekend) conditions.

Until these, and other, issues are addressed, generic “what-if” modeling exercises could be used to identify potentially significant factors governing the ozone weekend effect. Such exercises should address multiple hypotheses concerning the causes of the ozone weekend effect.

- **Emission inventory development**

Emission inventories for each day of the week are needed to help determine both the causes of the ozone weekend effect and the appropriate regulatory responses. Day-of-week emission inventories are particularly needed by computer models that might be used to simulate the ozone weekend effect. Various projects leading toward day-of-week inventories are already planned or currently in progress.

Is it realistic to expect the causes of the ozone weekend effect to be resolved?

Yes. With a realistic commitment of time and resources, the science, the data, and the analytical tools should converge to provide reasonably definitive answers concerning the ozone weekend effect. Furthermore, these same answers should clarify the relationship between periodic NO_x reductions on weekends and strategic NO_x reductions on all days. If so, the return on investment would be worthwhile.